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HOMOGENEITY OF CERAMICS: CORRELATION WITH MOLDING METHOD AND GEOMETRICAL PARAMETERS OF ARTICLES

A. I. Zakharov[1]

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The effect of the method of molding an intermediate ceramic article on its homogeneity is investigated considering samples of various shapes. A correlation is established between the degree of inhomogeneity of an intermediate article and its geometrical characteristics and molding conditions.

Production of ceramic articles in most cases is related to a modification of their size (shrinkage), which occurs nonuniformly over the article volume. Only preservation of relative homogeneity, i.e., the uniformity of properties of material in its different elementary volumes at such technological stages as molding, drying, and firing can produce an articles without distorting its prescribed shape (without deformation) and disturbances of continuity (micro- and macrocracks).

An admissible degree of heterogeneity, which does not produce defects, depends on the properties of initial materials, its treatment parameters, and the complexity of the shape of the article.

As early as at the stage of preparing a molding mixture, the intent is to obtain a sufficient degree of homogeneity, which may be a necessary, but not the only condition of obtaining a homogenous intermediate piece and later a homogenous finished product. Even with a good degree of mixing, the anisotropic shape of component particles can be a reason for particles in molding becoming oriented in certain directions (formation of texture). In this case, one can say that the intermediate article inherits the structure of some components (this happens in molding of clay-based mixtures).

Molding methods differ in the extent, surface area, and intensity of forces applied to material. In all molding methods pressure applied is unevenly distributed over the volume of the intermediate article due to external friction of material against the mold and partly due to internal friction between particles of the molding mixture.

The degree of homogeneity of intermediate and finished ceramics can be determined in different ways [1, 2]. Most researchers correlate the homogeneity of a molded piece with its uniform density and similarity of properties in different parts. The authors in [3 – 5] investigated nonuniform density of intermediate and finished products produced by various molding methods in metal molds and in slip casting and compared the molding methods with respect to reaching homogeneity. One should separately stress the role of the scaling factor due to a complex multiphase composition of ceramic materials [6].

To study the degree of homogeneity in intermediate products produced by various molding methods, one should use the notion of a degree of homogeneity, select a material represented by raw materials of different types, select molding methods that differ significantly with respect to the molding pressure values, and articles of different configurations.

The structure of most products of household and construction ceramics and the majority of refractory and engineering (functional, structural) ceramics is represented by crystalline phase grains of sizes ranging from 1 to 100 μm (close-grained ceramics). Selecting particle sizes for initial components within this range, we set the real scale of homogeneity. The most dispersed particles of the initial mixture were clay components of the porcelain mixture, and the coarsest grains were tags (indicators), namely, silicon carbide particles of grade "KCh – black silicon carbide" (fraction 63 – 80 μm). Silicon carbide particles were selected as tags due to their chemical inertia and different color, compared to other mixture components (black color against a white background).

A plastic molding mixtures, molding powder, and slip were prepared by thorough mixing of 90% porcelain mixture powder and 10% silicon carbide powder, moistening them to a required moisture level by standard laboratory techniques, including granulation by sieve screening, aging of mixture, and maturing of the slip.

Simultaneously with preparing a mixture with a silicon carbide additive, a reference mixture without additive was prepared.

[1] D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

TABLE 1

Molding method	Average value of parameter		
	moisture of intermediate article, %	density, kg/m^3	strength, MPa
Semidry molding:			
plates	4.69 ± 0.05	2.18 ± 0.01	24.1 ± 1.8
disks	3.51 ± 0.06	2.24 ± 0.01	–
Isostatic molding:			
plates	3.62 ± 0.06	2.22 ± 0.01	29 ± 1.3
disks	3.85 ± 0.04	2.24 ± 0.01	–
Plastic molding:			
plates	18.23 ± 0.14	2.29 ± 0.01	44.8 ± 1.5
disks	17.61 ± 0.11	2.28 ± 0.01	–
Slip casting, plates	–	2.24 ± 0.01	–

TABLE 2

Molding method	Average value of the degree of inhomogeneity for parameters			
	concentration of tags, rel. units	moisture of intermediate article, %	density, kg/m^3	strength, MPa
Semidry molding:				
plates	–	0.23	0.024	2.03
disks	38	0.19	0.020	–
Isostatic molding:				
plates	–	0.20	0.007	1.56
disks	27	0.07	0.011	–
Plastic molding:				
plates	–	0.42	0.017	3.54
disks	34	0.21	0.018	–
Slip casting:				
plates	–	–	0.011	–
disks	23	–	–	–

The degree of inhomogeneity σ of the resulting mixture, intermediate article, and finished ceramic article was estimated based on the mean quadratic deviation values [7]:

$$\sigma = \sqrt{\frac{\sum (x_i - x_{\mathrm{m}})^2}{N - 1}}\,, \tag{1}$$

where x_i is the concentration of tags in a test sample (the value of the parameter for a portion of the article); x_{m} is the mean arithmetic of the tag concentration (the value of the parameter for the whole article); N is the number of test samples.

Having determined the degree of inhomogeneity for the plastic mixture (molding powder, slip), it was used to mold articles in the shape of disks 30 mm in diameter and plates of size 40 × 30 mm by plastic molding (ramming the mixture into a gypsum mold), casting slip in a gypsum mold, semidry molding in a metal mold, and isostatic molding in a latex shell.

After molding, the disk-shaped articles were cut into 4 parts and the plate-shaped ones into 6 parts. The moisture of each part was measured and the concentration of tags was determined on a section using a binocular magnifying glass,

Dried and fired uncut articles were cut into the same number of parts using a diamond tool, and the mechanical strength and porosity of individual parts was identified. Each series consisted of at least 5 samples.

The results of measuring intermediate and finished ceramic samples are shown in Table 1.

Based on obtained results, one can note significant differences in the strength of the samples, which may be related to their inhomogeneity, however, mechanical strength as a property to a large extent depending on the density and structural specifics of materials, therefore, this property was not taken into account in the calculation of inhomogeneity.

Deviation in the values of properties, i.e., moisture of intermediate articles and concentration of tags in various parts of articles were determined according to formula (1). The degree of inhomogeneity calculated for each property was expressed in relative units (Table 2). The data in Table 2 generally corroborate the known facts: a high degree of homogeneity (the lowest values of mean quadratic deviation) are achieved in isostatic molding and slip casting. The obtained numeral values of the degree of inhomogeneity of samples made it possible to identify their dependence on the geometric characteristics of articles and the molding method.

We were primarily interested in the values of possible displacement of an elementary volume of material under compression, which is frequently accompanied by shear phenomena resulting in a nonuniform structure.

There is a formula known as the Balandin equation for pressure distribution across the height of a molded article:

$$p_h = p_0\, e^{-k\,(h/R_{\mathrm{h}})}, \tag{2}$$

where p_h is the pressure at the level h; p_0 is the pressure at the molding punch surface; k is the coefficient (twofold product of the lateral thrust and external friction coefficients); h is the distance from the molding punch; R_{h} is the hydraulic radius accepted as a ratio of the section surface area to the perimeter.

Equation (2) can be used to derive an expression for the degree of inhomogeneity (β < 1) of the molded article based on its height [8]:

$$\beta = e^{-k\,(h/R_{\mathrm{h}})}. \tag{3}$$

Expression (3) shows that there is no correlation between inhomogeneity of a molded piece and molding pressure and shows a crucial effect of the external friction coefficient. The shape factor in the equation is expressed in the ratio of the molded article height to the hydraulic radius calculated from the parameter, which also underlines the significance of external friction.

However, the authors in [3] report a linear variation of density along the height of a molded article (the Popil'skii – Smol' equation) and present data on a very complex depen-

dence of density distribution across a section perpendicular to the pressure direction. Thus, we cannot state that the dependence of inhomogeneity of an intermediate article on its geometric parameters and molding conditions has been uniquely established. Furthermore, in such molding methods as slip casting and isostatic molding the effect of the eternal friction factor is significantly lower, therefore, the role of molding pressure and the shape factor can be represented in a different way.

The geometric characteristics of an article are most easily described either by the ratio of its volume to surface, or by its characteristic thickness, which in this case will be equal to the height of the sample in the direction of molding. Let us accept the geometrical factors in the form of criterion G:

$$G = \frac{V}{F_m}, \quad (4),$$

where V is the sample volume; F_m is the surface area of the sample to which the molding force is applied.

This shape factor can be regarded as the height of the layer of material molded. The greater the value of G, the more difficult it is, presumably, to obtain a homogeneous material by applying the molding force to a limited area and overcoming external friction against the mold.

The molding force and the viscosity of the molded system are united in equations indicating dependence of the value of possible deformation on the force applied: from the Hooke equation for solid bodies and the Newton equation for ideal fluids to the power expressions for what is not as non-Newtonian fluids (Bingham body, Shvedov body, etc.). For an integrated evaluation of molding conditions, let us accept the factor S characterizing the molding conditions and the system characteristic:

$$S = \frac{P}{\eta_{rel}},$$

where P is the maximum molding pressure; η_{rel} is the relative viscosity of the system calculated from the volume part of the solid phase according to the Pivinskii expression for highly filled ceramics slips [8]:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \left(1 + \frac{K_S C_V}{1 - C_V / C_{V_{cr}}}\right)^2,$$

where η_0 is the viscosity of the dispersion medium (in our case $\eta_0 = 1$); C_V and $C_{V_{cr}}$ is the volume part of the solid compound in the suspension and its critical value (in our case $C_{V_{cr}} = 0.74$); K_S is the coefficient equal to 0.3.

The choice of Eq. (4) to characterize the viscosity of different systems (from slip to molding powder) has the following reason. First, this equation has been derived for thixotropic highly filled systems, which take an intermediate

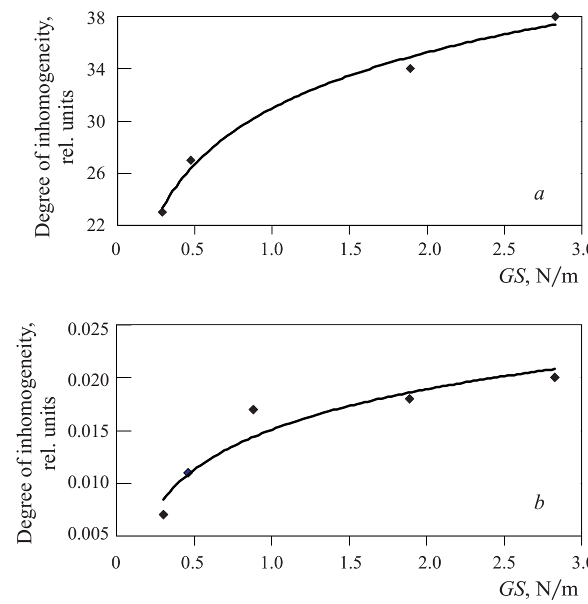

Fig. 1. The degree of inhomogeneity of test samples calculated based on the concentration of tags in various parts of intermediate product (*a*) and based on density of different parts (*b*) versus the product of factors G and S. Equations and degree of approximation reliability: *a*) $y = 30.987 + 6.1593\ln(x)$, $R^2 = 0.9871$; *b*) $y = 0.0151 + 0.0055\ln(x)$, $R^2 = 0.9145$.

position between plastic mixtures and slips, i.e., for systems with an intermediate (between coagulation and condensation) type of contacts. The molding powder of a porcelain mixture containing a substantial amount of argillaceous components can be regarded as well as a system with intermediate type of contacts. Second, expression (4) encompasses a maximum range of combinations of solid and liquid phases. By calculating the relative viscosity of the system using this equation, we obtained the following values: 3 for the slip, 11.3 for the plastic mixture, and 60 for the molding powder.

Having calculated the values of the factors characterizing the molding conditions, the characteristic of the system S, and the geometrical parameters of the article G, we determine the dependences (Fig. 1) between the product of these factors and the degree of inhomogeneity of the articles calculated from Eq. (1). The dimensionality of the product of the factors G and S is Newton per meter (N/m), which can be interpreted as a force gradient in the article arising as a consequence of nonuniform distribution of molding force over the article volume due to external and internal friction.

By analyzing inhomogeneity based on the density of samples after drying and firing, we took into account the fact that molding has the most perceptible effect on consolidation of a ceramic material.

It should be noted that dependences have been established for the degree of inhomogeneity calculated based on the density and tag concentration for various parts of the article; such dependences for strength and moisture have not been identified. We rejected considering strength as a homo-

geneity criterion for the reason explained above. The moisture of different parts of an article is presumably too much dependent on experimental conditions (extraction from the mold or shell, accuracy of section cut, etc.), therefore, is an unsuitable characteristic to estimate homogeneity of different parts of a molded article.

The dependence of the degree of inhomogeneity calculated based on a tag concentration in different parts of a molded article (disk-shaped) and density of different parts of articles (disk- and plate-shaped) molded by different methods, dried and, fired, on the product of factors S and G can be approximated with a sufficient degree of reliability by a logarithmic curve (Fig. 1).

The expression obtained after processing experimental data mentioned can be represented in the following form:

$$\sigma = C + k \ln (GS)$$

or, representing G as h in expression (2), i.e., as the height of the layer of material in molding:

$$\sigma = C + k \ln (V/F_{\mathrm{m}} P/\eta) = C + k \ln (h/F_{\mathrm{m}} T/\eta),$$

where C and k are coefficients; T is the molding force.

The resulting equation shows a nonlinear increase in the degree of heterogeneity in the mixture molded, as the factor of the article shape or the height of the layer of molded material increases and the ratio of pressure applied to the relative viscosity of the system grows. The factor S presumably has an interval of optimal values, and going beyond this interval makes molding inefficient or impossible (insufficient strength or defects).

The geometrical factors (or more precisely, the method of pressure application) has a deciding effect on inhomogeneity: its values vary from about 0.5 to 4.8, whereas the molding factor values vary insignificantly from 0.3 to 0.7. The values of the logarithm of the product of the factors resulted negative for such molding methods as isostatic molding and slip casting and positive for semidry and plastic molding.

The fact that the dependences of the degree of inhomogeneity quoted above tend to a certain limit can be accounted by the existence of physical bounds (mold walls) to the displacement of elementary volumes of material (including tangs) in a system of interrelated particles.

The obtained expression makes it possible to compare various molding methods for articles of different shapes with respect to reaching a certain degree of homogeneity. The volume of material molded is not such a significant factor as the surface area of molding pressure applied.

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